

**PCT**WORLD INTELLECTUAL PRO  
International

INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9605522A2

(51) International Patent Classification <sup>6</sup> : <b>G01V 3/14, G06K 19/12, G07D 7/00, G01R 33/44</b>		<b>A2</b>	(11) International Publication Number: <b>WO 96/05522</b> (43) International Publication Date: 22 February 1996 (22.02.96)
(21) International Application Number: <b>PCT/EP95/03157</b> (22) International Filing Date: 9 August 1995 (09.08.95)  (30) Priority Data: 110,597 9 August 1994 (09.08.94) <b>IL</b>  (71) Applicants (for all designated States except US): MICRO TAG TEMED LTD. [IL/IL]; Temed Industrial Park, 86800 D.N. Arava (IL). RAPAPORT, Erich, I. [AT/IL]; 29 Bezalet Street, 64683 Tel Aviv (IL).  (72) Inventors; and (75) Inventors/Applicants (for US only): ROSENFELD, Yuri [IL/IL]; 228/2 Neve Nof, Yeroham (IL). GILL, David [IL/IL]; 12 Rakanati Street, Tel Aviv (IL). GOLDFELD, Lev [IL/IL]; 14/3 Israel Yeshayahu, Beer Sheva (IL). SHAMES, Alexander [IL/IL]; 4/2 King Azzaya, Beer Sheva (IL). LYANDRES, Vladimir [IL/IL]; 8 Dov Yosef Street, Beer Sheva (IL).  (74) Agent: VOSSIUS & PARTNER; Siebertstrasse 4, D-81675 München (DE).		(81) Designated States: AU, BR, CA, JP, NO, NZ, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>	
(54) Title: METHOD FOR LABELING, VERIFICATION AND/OR IDENTIFYING AND DEVICE FOR IMPLEMENTING SAID METHOD			
(57) Abstract <p>The invention relates to a method of labeling, authenticating and/or identifying a paper, credit/identification card, bank note, article or any other object using both nuclear magnetic resonance in magnetically ordered materials and nuclear quadrupole resonance phenomena as well as other phenomena of electric/magnetic dipole or tunnel transitions between Stark-Zeeman sublevels, frequencies of which belong to the radio-frequency band. These methods being characterized in that a minor amount of at least one authenticating substance is added to the object, said substance having a strong unique and identifiable response in radio-frequency domain at room temperature, with the spectroscopy being performed in the absence of any supported external static field, and with any specific response (intensity, line width, line shape, splittings, free induction decay, spin echoes or their combinations) being used as a criterion for discrimination. The spectroscopy being performed in time domain (pulse) or frequency domain (continuous wave) with or without intensity, polarization, frequency or any other modulation of the exciting electromagnetic field. The invention also provides instruments for implementing the method, and a set of substances usable with the method.</p>			

Single Detectable Marker

Probe head

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METHOD FOR LABELING, VERIFICATION AND/OR IDENTIFYING  
AND DEVICE FOR IMPLEMENTING SAID METHOD

The invention relates in general terms to the field of labeling, authenticating or identifying, and more particularly it relates to new methods of verifying the authenticity of objects and/or identifying them as well as electronic article surveillance (theft prevention etc.) and personnel verification; new instruments for implementing these methods; and new substances adapted to the corresponding methods and instruments. The term "substance" is used to cover any substance or composition of substances capable of being applied on the surface or into the bulk of an arbitrary object, locally or diffusely e. g. like an ink, dye, glue, powder, film, wire, foil or adhesive label.

Numerous techniques are already known for authenticating papers of value, or the like, with the aid of spot reactions (Dutch patent application No. 6613250) or fluorescence (French Pat. Nos. 2,289,976; U.S. Pat. No. 4,146,792).

A variety of electronic surveillance of goods or personnel verification systems currently exists. They involve detection of macroscopic magnetic properties (US Patent No. 5,146,204) or macroscopic resonance associated with LC electrical circuit resonance (U.S. Pat. No. 4,870,391; Japanese Patent No. 4,800,369; Dutch Patent No. 5,068,641; U.S. Pat. No. 5,081,045; Dutch Patent NO. 5,051,727),

or bulk mechanical vibration resonance, or nonlinear electrical transponders or high permeability magnetically saturated soft magnetic elements.

The first patent claimed the application of electron paramagnetic resonance (EPR, also known as electron spin resonance - ESR) to the problems of authenticating or identifying papers of value was U.S. Pat. No. 4,376,264. It teaches the use of substances having EPR characteristics detected by high field EPR in microwave band (from 9 GHz). U.S. Pat. No. 5,149,946 claims the use of ESR in radio-frequency band for solving the same problem. U.S. Pat. No. 5,175,499 claims decision of the authenticating problem with the help of such magnetic resonance phenomena as nuclear magnetic resonance (NMR), electron spin resonance (ESR), ferromagnetic resonance (FR), ferrimagnetic resonance (FER), antiferrimagnetic resonance (AFER), domain wall resonance (DWR), spin wave resonance (SWR), spin-echoes (SER).

All of the aforementioned patents are based on a variety of magnetic resonance phenomena. These phenomena are associated with nuclear, electron, atomic or molecular magnetic dipole moments acting individually or cooperatively in the presence of external magnetic fields to give nuclear magnetic resonance (NMR), electron

spin/paramagnetic resonance (ESR, EPR), ferromagnetic resonance etc. The magnetic resonance is exhibited when the dipole moments precessing in the magnetic fields absorb and re-radiate microwave or radio-frequency electromagnetic radiation at or very close to the precession frequency. The serious disadvantage of applying aforementioned phenomena to the purposes of authenticating and/or identifying objects is necessity of external static magnetic field for the excitation and detection of resonance response. This magnetic field can be supplied either as a large field over the entire interrogation volume, or by a small permanent or semi-permanent magnet placed close to the resonant material and carried round with it and the object. For getting resonance responses with high sensitivity and high resolution the said field should be strong (about or more than 0.01 T) and omogeneous. These demands make both the marker/label and instrument design complicated. Otherwise, the presence of strong external magnetic field within the interrogation volume or near the marker runs the risk of any health damage (peacemakers etc.) as well as the risk of wiping out data contained on magnetic media; all this makes it impossible for identifying credit or bank cards.

There is a variety of phenomena having the same microscopic nature as aforementioned magnetic resonance phenomena, but

their macroscopic manifestation is absolutely different. First of all, they do not need any external static electrical or magnetic field (either within the interrogation zone or locally from a supporting substrate) for getting a detectable resonance response after radio-frequency or microwave irradiation. These phenomena can be classified as mixed electron-nuclear resonances in which the precession of nuclear electric or magnetic dipole moments is provoked by cooperative or individual electron subsystem. Strong polarization of exchange coupled electron spins or gradient of electric field lead to the splittings of degenerate Stark-Zeeman sub levels between which a lot of allowed and "forbidden" transitions exists. The main distinctive feature of these resonances is the possibility of exciting a detectable resonance response in a resonant material (label, marker) exposed only to electromagnetic radiation at the resonance frequency. The presence of the external static electric or magnetic field (both within the whole interrogation volume and locally due to the magnetic material of the substrate) is not a necessary condition for receiving a detectable signal. In some cases the presence of the external field (which, for example, may be many times stronger than Earth' magnetic field) may prevent the detection of the signal.

The phenomena of nuclear magnetic resonances (NMR) in magnetically ordered materials (ferromagnets, antiferromagnets, ferrimagnets) are associated with the splitting of nuclear Zeeman sub levels by strong hyperfine field which is induced by magnetically ordered electron subsystem. The strong resonances are observed from both host and doped nuclei possessing non-zero nuclear magnetic moments such as  $^{55}\text{Mn}$ ,  $^{57}\text{Fe}$ ,  $^{59}\text{Co}$  etc. included into magnetically ordered metals, alloys, coordination or organic compounds. Every resonance frequency is unique for the chosen resonant substance and belongs to the radio-frequency waveband and, as a rule, are not greater than 1 GHz.

The phenomenon of nuclear quadrupole resonance (NQR) is associated with the splitting of nuclear sub levels by the gradient of electric field which is induced by molecular electrons. This resonance is observed in both host and doped nuclei possessing non-zero quadrupole nuclear moment such as  $^{11}\text{B}$ ,  $^{35}\text{Cl}$ ,  $^{75}\text{As}$ ,  $^{79,81}\text{Br}$ ,  $^{127}\text{I}$  etc. The observed resonance frequencies are the same as in the previous paragraph.

A lot of resonances dealt with different dipole and tunnel transition between degenerate Stark-Zeeman sub levels also shows strong responses after excitation in radio-frequency

or microwave band at the absence of any external static field. Typical substances demonstrated such resonances are the large class of coordination compounds with mixed valence or so-called Jahn-Teller crystals.

For convenience, the term "zero external static field radio-frequency resonance" will be used herein to include all of these magnetic and spin phenomena. The term "zero external field" being applied to aforementioned resonances implies herein that such resonances can be observed at the absence of any external static field or at very weak external static field like Earth' magnetic field (0.5 mT). There it is worthwhile to mention that this weak field is not necessary demand for resonance effect but does not prevent the effect. The term "radio-frequencies" covers herein the electromagnetic frequency band from 1 MHz to some GHz and, as a rule, are not greater than 1 GHz. The term "room temperature covers herein the temperature range of common working conditions both lower and upper 0o C which does not require special cooling to cryogenic temperatures or heating to high ones.

From the point of view of its technical implementation the phenomenon of very low field electron spin resonance (VLF ESR) is very close to named zero-field resonances. Newly



developed paramagnetic substances such as ion-radical salts, lithium phthalocyanin or gamma-irradiated fused quartz gave the possibility to observe ESR at very low external magnetic fields (about 1 mT and less) with sufficient sensitivity. It means that an instrument includes only means for scanning and modulation of the Earth' magnetic field to reach the point of resonance but not for generation of static supported field. This feature is the main distinctive difference from the methods and instruments which was claimed in cited US Patents No. 5,149,946 and No. 5,175,499. This effect is also observed in radio-frequency waveband.

Substances exhibiting zero-field resonance phenomena described above can be used in accordance with this invention for object labeling, authenticating and/or identifying and applied for anti-forgery, anti-pilferage or security surveillance. Such use is possible because they can have extremely strong, unique and well defined resonances in radio frequency domain at room temperature, with the spectroscopy being performed in the absence of any artificial external static fields, and with any specific response being used a criterion of discrimination. These responses may be used to indicate the presence or identity of the labeled object. This can be achieved in a preferred embodiment of the invention by the use of radio-frequency

interrogation system which also detects an increase in the absorption of the interrogating electromagnetic energy or re-emission of electromagnetic energy by labeling substance at the resonance frequency.

According to the first aspect of this invention, there is provided a method of labeling, authenticating and/or identifying an object using zero external static field radio-frequency resonance phenomena where said phenomenon is either nuclear magnetic resonance in ferromagnets, or antiferromagnets, or ferrimagnets, or nuclear quadrupole resonance, or very low field electron spin resonance, or said resonance phenomenon is due to electric/magnetic dipole or tunnel transitions between Stark-Zeeman sub levels, or any combinations of aforementioned phenomena.

According to the second aspect of this invention the aforementioned effects take place in ferromagnetic metals, alloys, coordination or organic compound including at least one type of nuclei with non-zero nuclear spin, or antiferromagnetic ones including at least one type of nuclei with non-zero nuclear spin, or ferrimagnetic ones including at least one type of nuclei with non-zero nuclear spin, or metals, alloys, coordination or organic compound including at least one type of nuclei with non-zero electric quadrupole moment, or organic radical compound

like nitroxides, recrystallized diphenylpicryl hydrazyl, ion-radical salts, lithium phthalocianin, or gamma-irradiated fused quartz, or inorganic salt or coordination compound including paramagnetic ions of transition or rare earth groups, or coordination compound with mixed valence, or so-called Jahn-Teller crystals wherein all mention substances may be in the form of crystalline solid, polycrystalline solid, amorphous solid, wire, foil, liquid.

According to the third aspect of this invention, substance capable of being applied to the object locally or diffusion alloy, outside or inside the object in the form of ink, dye, glue, film, wire, foil, any adhesive label, is used for authenticating and/or identifying of papers of values, documents, bank notes, checks, credit cards, bank cards, identification cards, tags, keys, diskettes, and also are used for electronic articles surveillance (theft prevention in shops, stores, libraries etc.) and personnel verification, or for security or custom surveillance when the labeled object presents jewelry, explosive, arm or drug.

According to the fourth aspect of this invention the instruments for implementing of the presented method for authenticating and/or identifying of papers of values,

documents, bank notes, checks, credit cards, bank cards, identification cards, tags, keys, diskettes, comprise a system generating continuous or pulse, modulated or non modulated emitting radiation in the radio frequency band, including generator of continuous or pulse modulated or non modulated radio frequency signal and emitting probe head or coil, transforming it in electromagnetic radiation, and system for detection of the re-radiation emitted by the resonant substance in response to the said radio frequency radiation, including receiving probe head or coil and detection device with registration device fixing presence of the re-radiation from the resonant substance. In some of these instruments the same probe head or coil is used as for emitting of the radiated signal as well as for receiving of reradiation of the resonant substance. For electronic articles surveillance (theft prevention in shops, stores, libraries etc) and personnel verification, or for security or customs surveillance when the labeled object presents jewelry, explosive, arm or drug, the instruments for implementing of the presented method are built as aforementioned system, wherein gates located at a point of control in shop, store, library, post office, airport or custom office are used instead probe head or coil.

According to the fifth aspect of this invention the proposed method can be used for detection of the labeled object (for example, electronic articles surveillance), if a single one resonant substance label is used, or for identification/recognition of the labeled object if a plurality of readable markers produced by a single one resonant substance, spatially disposed in a well determined manner like a bar code, strip code etc. Identification of the labeled object is realized also if a plurality of resonant substances comprising marker provides a set of well resolved responses in frequency or time domains. The proposed identification marker containing a plurality of resonant substances or locally distributed single resonant substance are used together with other data storage methods (magnetic or optic recording etc.) providing a mean (key word or key number) for decoding information recorded by these methods.

According to the sixth aspect of this invention labeling of the object of authenticating and/or identifying is achieved by introducing of the resonant substance in ink, dye, glue or other liquid substance before printing on the surface of the labeled object (bank notes, documents, tags etc.), or into the bulk of the labeled object (paper, plastic, explosive or any package material) during its production or packaging. The substance is being introduced

locally or diffusely in special adhesive label, and for destroying prevention may be visually masked if it is necessary.

According to the seventh aspect of this invention the resonant substance used for the object labeling is neutralized if it is necessary (for example in anti-theft application) by alteration of physical properties of the substance (for example, by magnetizing, heating etc.) or by alteration of chemical properties of the substance (for example, by oxidation, reduction etc.) or by electromagnetic screening of the resonant substance, or by removing the resonant substance together with supported tag, adhesive label etc. (for example by mechanical removal or by evaporation of the resonant substance together with supported tag by its local heating).

According to the eighth aspect of this invention zero external static field radio-frequency resonance phenomena are used for the amplification of LC electrical circuit resonance applied for electronic articles surveillance systems which currently exist, by producing of the said LC circuit from the resonant substance with the same resonance frequency, or by covering/adjusting of the said LC circuit by/to the resonant substance with the same resonance frequency.

According to the ninth aspect of this invention for protection of the authenticating and/or identifying system masking of the system resonant frequencies by emission of electromagnetic radiation at random frequencies including the working resonance is used, and for secrecy providing of resonant properties of the labeling substance the letter is placed together with any deactivation substance acting in the case of any unauthorized access to the said substance (for example, by strong oxidation in the air etc.).

For better understanding of the present invention, the preferred embodiments will now be described by way of examples, with reference to the accompanying drawings in which:

FIG. 1a, 1b show examples of configurations of a detectable marker, single and spatially disposed correspondingly (bar code).

FIG. 2 shows schematically identification and/or authentication continuous wave performance system using for use with object, label or marker including resonant substance.

FIG. 3 shows graph of the dependence of electromagnetic field absorption intensity on frequency applied to the labeled object.

FIG. 4 shows schematically identification and/or authentication pulse performance system using re-radiating label with registration of Free Induction Decay (FID) signal.

FIG. 5 shows a schematic time diagram of the exciting and FID signals.

FIG. 6 shows schematically identification and/or authentication pulse performance system using re-radiating label with registration of Spin Echo Signal (SES).

Fig. 7 shows a schematic time diagram of the exciting pulses and SES.

Referring first to FIGS. 1a and 1b two examples of possible configuration of a detectable marker or label are shown. In FIG 1a a label with spot concentrated resonant substance is shown. Such labels are used in simple detection systems (for example, in any paper verification). If the labeled object is moved through probe head the re-radiation signal from resonant substance is detected and so authentication of the labeled object is performed. In FIG. 1b a label with spatially disposed resonant substance like bar code is shown.



Such labels are used in the systems of objects identification (for example in systems of identification of credit cards). If the labeled object is moved through probe head the re-radiation signals from every stripe of bar code are read separately and so registration of the code and identification of the object is performed.

FIG. 2 shows schematic example of continuous wave identification and/or authentication system using label including any resonant substance. Referring to FIG. 2, CG represents generator performing control of the resonant frequency of LC circuit. LA represents linear amplifier of the signal at resonance frequency. NLA represents non-linear amplifier limiting amplitude of the signal. D represents detector and RD represents registration device. The device records absorption of electromagnetic radiation by resonant substance.

FIG. 3 shows graphs of the dependence of electromagnetic field absorption intensity upon the frequency of the applied electromagnetic radiation. The graph magnitude represents maximal level of absorption of electromagnetic field, the horizontal axis shows frequency,  $\omega_r$  is resonance frequency of corresponding substance.

FIG. 4 shows schematically an example of identification and/or authentication pulse performance system using re-radiating label with registration of FID signal. Referring to FIG. 4, CG represents controlled generator, SW represents electronic switch, PA represents power amplifier, HFA represent high frequency amplifier, FM represents frequency mixer, IFA represents intermediate frequency amplifier, PD represent phase detector, LFA represents low frequency amplifier, RD represents registration device, CPG represents pulse generator, PH represents probe head.

FIG. 5 shows a schematic diagram of the exciting and FID signals. The rectangular pulse represents envelope of the exciting high frequency signal, decayed line represents FID signal, and the solid line represents envelope of the recorded signal, the horizontal axis shows time,  $t_{EP}$  represents length of the exciting pulse,  $t_{DT}$  represents time interval (dead time), where registration of FID signal is impossible due transient processes,  $t_R$  is an interval of the FID signal registration.

FIG. 6 shows schematically the example of identification and/or authentication pulse performance system using re-radiating label with registration of Spin Echo Signal (SES). HFG represents high frequency generator, CPG

represents control pulse generator, SW1 and SW2 represent electronic switches, HFPA represents high frequency pulse amplifier, RPH represents resonant probe head, ESA represents echo-signals amplifier, PD represents phase detector, LFA represents low frequency amplifier, CWD represents detector with controlled window, RD represents registration device.

Fig. 7 shows a schematic diagram of the exciting pulses and SES.

Sequence of rectangular pulses represents envelope of exciting signal, dotted line represents envelope of FID signal, triangular pulse represents spin echo signal, the horizontal axis shows time,  $t_{P1}$  represents time length of the first exciting pulse,  $t_{P2}$  represents time length of the second exciting pulse,  $t$  represents an interval between exciting pulses as well as between the last exciting pulse and the maximum of the spin echo signal. The value of  $t$  should be less than the value of transversal relaxation time  $T_2$  for the electron or nucleus in chosen resonant substance.

The invention will be illustrated further in non-limiting fashion by the following Examples.

#### EXAMPLE 1

This example describes the construction of continuous wave identification and/or authentication system using label including resonant substance. The system (FIG. 2) represents voltage radio frequency generator including controlled LC circuit, sequentially connected LA, NLA, from which output signal through feedback circuit including balance resistor R enters input of LA. Resonance frequency of LC circuit linearly changes in the fixed range with help of varicond under control of pulses from output of CG. Output of LA is connected also with RD through D. If the label with resonant substance is brought in the coil of LC, the quality factor of LC decreases. As it is clear from FIG. 3 at the frequency equal to the resonant frequency of the label substance, intensity of the electromagnetic field absorption achieves maximum, the quality factor of LC circuit decreases abruptly and generation is interrupted. This fact is registered by two connected blocks D, RD and in such a way detection of the labeled object is performed.

## EXAMPLE 2

This example describes the construction of identification and/or authentication pulse performance system using re-radiating label with the registration of FID signal. In this example a powdered sample (average particle diameter  $d$  is about  $2\text{ }\mu\text{m}$ ) of manganese ferrite ( $\text{MnFe}_2\text{O}_4$ ) was chosen as a resonant substance. The resonance frequency is  $536\text{ MHz}$  at Earth' magnetic field and room temperature ( $300\text{ K} \pm 20\text{ K}$ ). The label was designed according to Fig. 1a. About  $200\text{ mg}$  of resonant substance was concentrated in a  $3\text{ mm} \times 20\text{ mm} \times 0.5\text{ mm}$  strip included into the bulk of plastic bank card. The probe head (PH) is circular surface coil designed as a single turn of  $14\text{ mm}$  in diameter wound from  $2\text{ mm}$  copper wire, tuned to resonance frequency and matched to  $50\text{ }\Omega$ . Referring to Fig. 4 the system includes transmitting block consisting from sequentially connected CG and SW, which the first output is connected through PA with radiation coil of PH, and the second output of SW is connected with the FM control input of receiving block consisting from the sequentially connected receiving coil of PH, HFA, FM, IFA, PD, LFA and RD, and also control pulse generator CPG, connected with the FM control inputs of CG, SW and PD. During absence of the control pulse from CPG output, CG produces voltage oscillations with the frequency  $f_0 = 536\text{ MHz}$  entering radiation surface coil of PH through

the first output of SW and PA. During existence of the pulse at the output of CPG, working frequency of CPG changes from  $f_0$  to  $f = f_0 + f_{IF}$ , where  $f_{IF} = 10.7$  MHz is the intermediate frequency of the receiving block, and signal of CG enters through the second output of SW the FM control input of receiving block. The same pulse of CPG opens PD of the receiving block. So time separation of transmitting and receiving blocks functioning is performed, which protects system from the false registration of the identified object due to infiltration of the transmitted signal at the receiving block input. Bringing of the lab 1 near the plane of the PH surface coil there appears FID signal (with envelope shown in Fig. 5) which through receiving coil of PH, HFA, FM, IFA enters PD, opened by the pulse of CPG. Output signal of PD is registered by RD and in such a way detection of the labeled object is performed. The one pulse sequence is repeated with the delay time  $\tau_{DEL} = 10 \mu s$  being adjusted to gain the best signal to noise ratio ( 130% for circular surface coil at  $\tau_{DEL}$  is greater or about of  $0.05 \times T_1$ ) where  $T_1 = 130 \mu s$  is the longitudinal relaxation time for the  $^{55}\text{Mn}$  nucleus is powdered manganese ferrite at Earth' magnetic field and room temperature.

## EXAMPLE 3

This example describes the construction of identification and/or authentication pulse performance system using re-radiating label with registration of spin echo signal (SES). Referring to FIG. 6, the system includes transmitting block consisting sequentially connected HFG, SW1, which the first output is connected through HFGA with RPH, which through SW2 is connected with the receiving block, consisting from sequentially connected ESA, PD, which control input is connected with the second output of SW1, and output of PD is connected with RD through LFA, CWD. Functioning of the transmitting and receiving blocks are controlled by CPG, which first output is connected with control input of SW1, which second output is connected with control input of SW2, and the third output is connected with control input of CWD. HFG produces continuous harmonic high frequency signal, entering input of SW1. CPG produces special pulse sequence (FIG. 7), modulating signal of in SW1, from which output sequence of radio pulses is amplified in HFGA, and enters HRP. During presence of the control pulse from CPG output, SW2 breaks connection between RPH and receiving block, so signal emitted by transmitting block does not enter receiving block. Except this, as it is clear from FIG. 6, during

existence of the said pulse sequence, there are no reference signals at the control input PD, and CWD is closed. All this provides protection of the system from the false registration of the identified object due infiltration of the transmitted signal at the receiving block input. After end of the specific pulse sequence SW1 and SW2 change their positions and the reference signal through SW1 enters the control input of PD, and correspondingly, RPH signal enters ESA of the receiving block. Except this impulse from the third output of CPG opens CWD. After two pulse radiation the label re-radiates spin echo signal (FIG. 7) which is registered by RD of the receiving block and in such a way detection of the labeled object is performed. The two pulse sequence is repeated with the delay time being adjusted to prevent the saturation of SES ( $t_{DEL} > 5T_1$ ).

The invention relates to a method of labeling, authenticating and/or identifying a paper, credit/identification card, bank note, article or any other object using both nuclear magnetic resonance in magnetically ordered materials and nuclear quadrupole resonance phenomena as well as other phenomena of electric/ magnetic dipole or tunnel transitions between Stark-Zeeman sub-levels, frequencies of which belong to the radio-frequency band. These methods being characterized in that a minor amount of at least one authenticating substance is added to



the object, said substance having a strong unique and identifiable response in radio-frequency domain at room temperature, with the spectroscopy being performed in the absence of any supported external static field, and with any specific response (intensity, line width, line shape, splittings, free induction decay, spin echoes or their combinations) being used as a criterion for discrimination. The spectroscopy being performed in time domain (pulse) or frequency domain (continuous wave) with or without intensity, polarization, frequency or any other modulation of the exciting electromagnetic field. The invention also provides instruments for implementing the method, and a set of substances usable with the method.

CLAIMS:

1. A method of labeling, authenticating and/or identifying an object using zero external static field radio-frequency resonance phenomena, characterized in that a minor amount of at least one authenticating substance is added or applied to the object, said substance having a strong unique and identifiable response in a radio-frequency domain at room temperature, by means of spectroscopy performed in the absence of any external static field, and where any specific response is used as a criterion for discrimination.

2. A method as claimed in claim 1, wherein said resonance phenomenon is nuclear magnetic resonance (NMR) in ferromagnets.

3. A method as claimed in claim 1, wherein said resonance phenomenon is nuclear magnetic resonance (NMR) in antiferromagnets.

4. A method as claimed in claim 1, wherein said resonance phenomenon is nuclear magnetic resonance (NMR) in ferrimagnets.

5. A method as claimed in claim 1, wherein said resonance phenomenon is nuclear quadrupole resonance (NQR).

6. A method as claimed in claim 1, wherein said resonance phenomenon is very low field electron spin resonance (VLF ESR).

7. A method as claimed in claim 1, wherein said resonance phenomenon is due to electric/magnetic dipole or tunnel transitions between Stark-Zeeman sub levels.

8. A method as claimed in claim 1, wherein at least two phenomena claimed in claims 2-7 are used simultaneously.

9. A method as claimed in any of claims 1 to 8, wherein said object is paper, paper of value, bank note, check, credit card, bank card, identification card, passport, tag, key, diskette or special adhesive label.

10. A method as claimed in any of claims 1 to 9, wherein said object is an article applied to an electronic product surveillance for theft prevention in shops, stores, libraries etc.

11. A method as claimed in any of claims 1 to 9, wherein said object is a special tag, label or marker and the method is applied for personnel verification.
12. A method as claimed in any of claims 1 to 9, wherein said object is a document, jewel, arm, explosive or drug, said method being applied for security or customs surveillance.
13. A method as claimed in claim 2, wherein said substance is a ferromagnetic metal, alloy, coordination or organic compound including at least one type of nuclei with non-zero nuclear spin.
14. A method as claimed in claim 3, wherein said substance is a antiferromagnetic metal, alloy, coordination or organic compound including at least one type of nuclei with non-zero nuclear spin.
15. A method as claimed in claim 4, wherein said substance is a ferrimagnetic metal, alloy, coordination or organic compound including at least one type of nuclei with non-zero nuclear spin.

16. A method as claimed in claim 5, wherein said substance is metal, alloy, coordination or organic compound including at least one type of nuclei with non-zero electric quadrupole moment.

17. A method as claimed in claim 6, wherein said substance is an organic radical compound like a nitroxide, recrystallized diphenyl picryl hydrazyl, an ion-radical salt or lithium phthalocyanin.

18. A method as claimed in claim 6, wherein said substance is gamma-irradiated fused quartz.

19. A method as claimed in claim 6, wherein said substance is an inorganic salt or coordination compound containing paramagnetic ions of transition or rare earth groups.

20. A method as claimed in claim 7, wherein said substance is a coordination compound with mixed valence.

21. A method as claimed in any of claims 1 to 20, wherein said substance is a crystalline solid, polycrystalline solid, amorphous solid, wire, foil, liquid.

22. An instrument for implementing the method claimed in any of claims 1 to 21, which instrument comprises a probe head or coil,

which probe head comprises means for continuous emission of radiation in the radio-frequency band; and means for detecting radiation emitted or absorbed by the resonant substance in response to said radio-frequency radiation.

23. An instrument for implementing the method claimed in any of claims 1 to 21, which instrument comprises a gate which,

in use, will be located at a point of control in a shop, store, library, post office, airport or custom office, which gate comprises means for continuous emission of radiation in the radio-frequency band; and means for detecting radiation emitted by the resonant substance in response to said radio-frequency radiation.

24. An instrument as claimed in claims 22 and 23, wherein said means for emitting radio-frequency radiation is arranged to emit pulses of radiation.

25. An instrument claimed in any of claims 22 to 24, which instrument comprises means for generating modulation electromagnetic field across the probe head, coil or gate.

26. A method as claimed in any of claims 1 to 21, for data storage or encoding/decoding purposes which comprises providing a plurality of readable markers of the resonant substance, spatially disposed in a well-determined manner, like a bar code, strip code etc.

27. A method as claimed in claim 1, for data storage or encoding/decoding purposes by means of a method claimed in any of claims 2 to 7 and, correspondingly, resonant substances claimed in any of claims 13 to 20, which provide a set of well-resolved responses in frequency or time domain.

28. A method of data storage or encoding/decoding, said method being a combination of the methods claimed in claims 26 and 27.

29. A method as claimed in any of claims 26 to 28, wherein said method is applied together with other data storage methods (magnetic or optic recording etc.) provides means (key word or key number) for decoding information recorded by another method.

30. An instrument for implementing the method claimed in any of claims 26 to 29, which instrument comprises a probe head or gate, which probe head comprises means for generating continuous or pulsed radiation, of at least

one radio-frequency; means for detecting radiation emitted or absorbed by the resonant substance in response to said radio-frequency radiation; means for scanning said radiation or object spatially as well as means for analysis of spatially or spectrally distributed responses.

31. A method as claimed in any of claims 1 to 21 and 26 to 29, wherein said substance is introduced into ink, dye, glue or other substance before printing on the surface of an object (bank note, document, tag etc.) to be labeled.
32. A method as claimed in any of claims 1 to 21 and 26 to 29, wherein said substance is introduced into the bulk of labeled object (paper, plastic, explosive) and/or its packaging material during object production and/or packaging.
33. A method as claimed in any of claims 1 to 21 and 26 to 29, wherein said substance is introduced in ink, dye, glue or other substance before covering the surface of labeled object.
34. A method as claimed in any of claims 1 to 21 and 26 to 29, wherein said substance is introduced locally or diffusely in special adhesive label.



35. A method as claimed in any of claims 1 to 21, 26 to 29 and 31 to 34, wherein said substance is visually masked.

36. A method of deactivation of resonant properties of substances claimed in claims 13-21 by an alteration of physical properties of the substances.

37. A method of deactivation of resonant properties of substances claimed in claims 13-21 by an alteration of chemical properties of the substances.

38. A method of deactivation of resonant properties of labels or markers containing substances claimed in claims 13-21, by electromagnetic screening of the resonant material.

39. A method of deactivation of resonant properties of labels or markers containing substances claimed in claims 13-21, by removing resonant material together with supported tag, adhesive label etc.

40. A method of amplification of LC electrical circuit resonance used for electronic article surveillance systems,  
by producing said LC circuit from

the resonant substance claimed in claims 13-21, having the same resonance frequency.

41. A method of amplification of LC electrical circuit resonance used for electronic article surveillance systems, by covering/adjusting said LC circuit by/to the resonant substance claimed in claims 13-21, having the same resonance frequency.

42. A method of masking of working resonance frequency for instruments claimed in claims 22 to 25 and 30, wherein said electromagnetic radiation is emitted at frequencies randomly generated by transmitter including the resonance frequency.

43. A method for providing secrecy of resonant properties of substances used in the method claimed in claims 1 to 21, 26 to 29 and 31 to 42, wherein said substance is placed together with any deactivation substance which acts in the case of any unauthorized access to said substance.

44. A method for providing secrecy of resonant properties of substances used in the method claimed in claims 1 to 21, 26 to 29 and 31 to 43, wherein said substance is mixture of at least two modifications with the same chemical composition which exists in different structural phases (or isomorphic) and only one of them give response at resonance frequency.
45. A method for providing secrecy of resonant properties of substances used in the method claimed in any of claims 1 to 21, 26 to 29 and 31 to 44, wherein said substance gains its resonant properties at the resonance frequency only at the same time with local (at the point of said substance location) heating/cooling or magnetization/demagnetization.

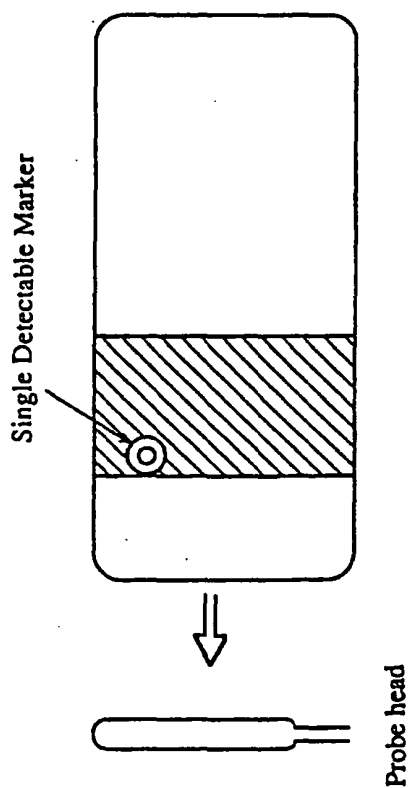


Fig. 1a

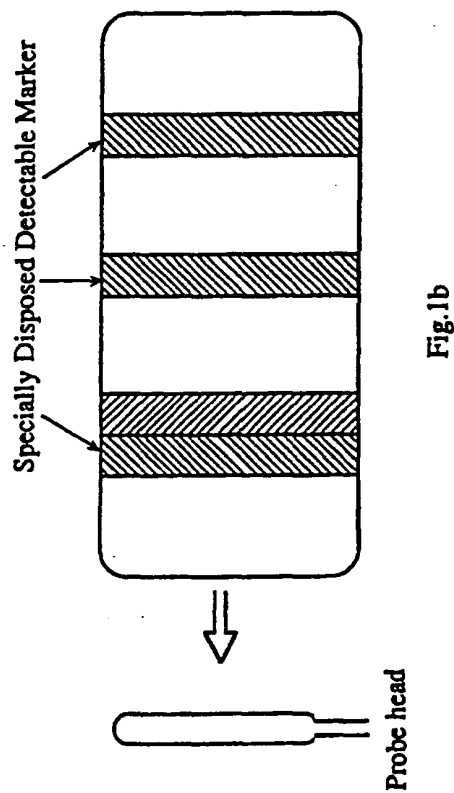


Fig. 1b

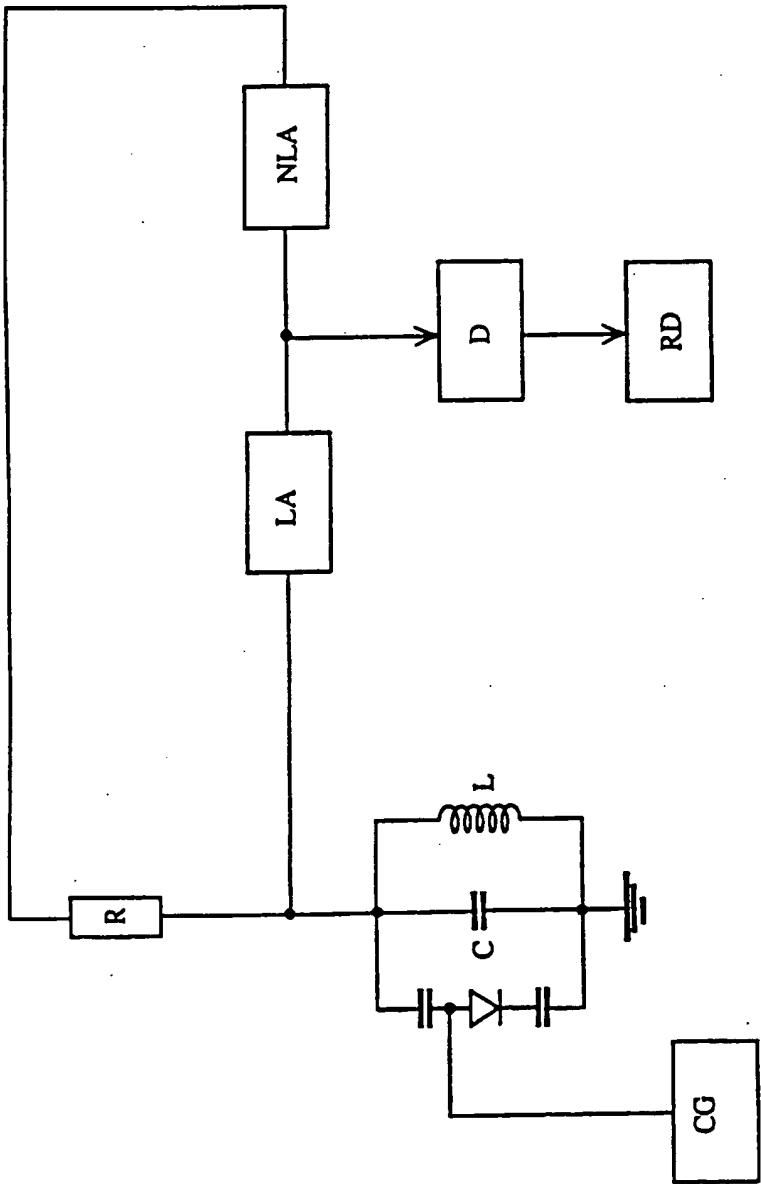


Fig.2

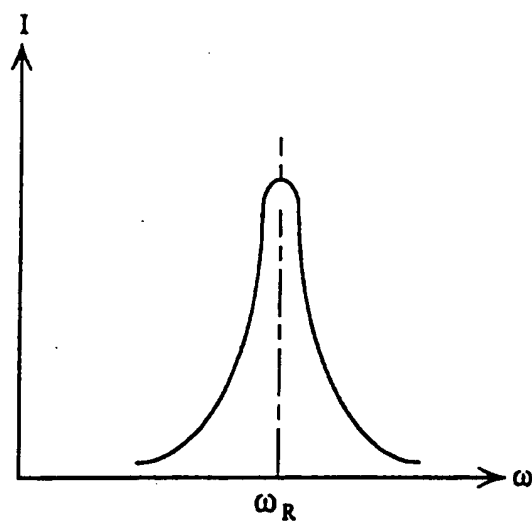


Fig.3

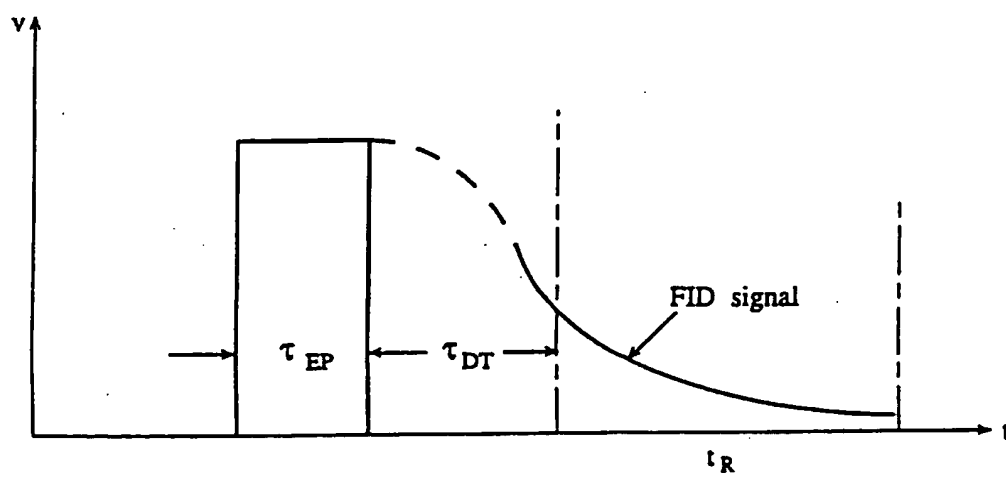


Fig.5

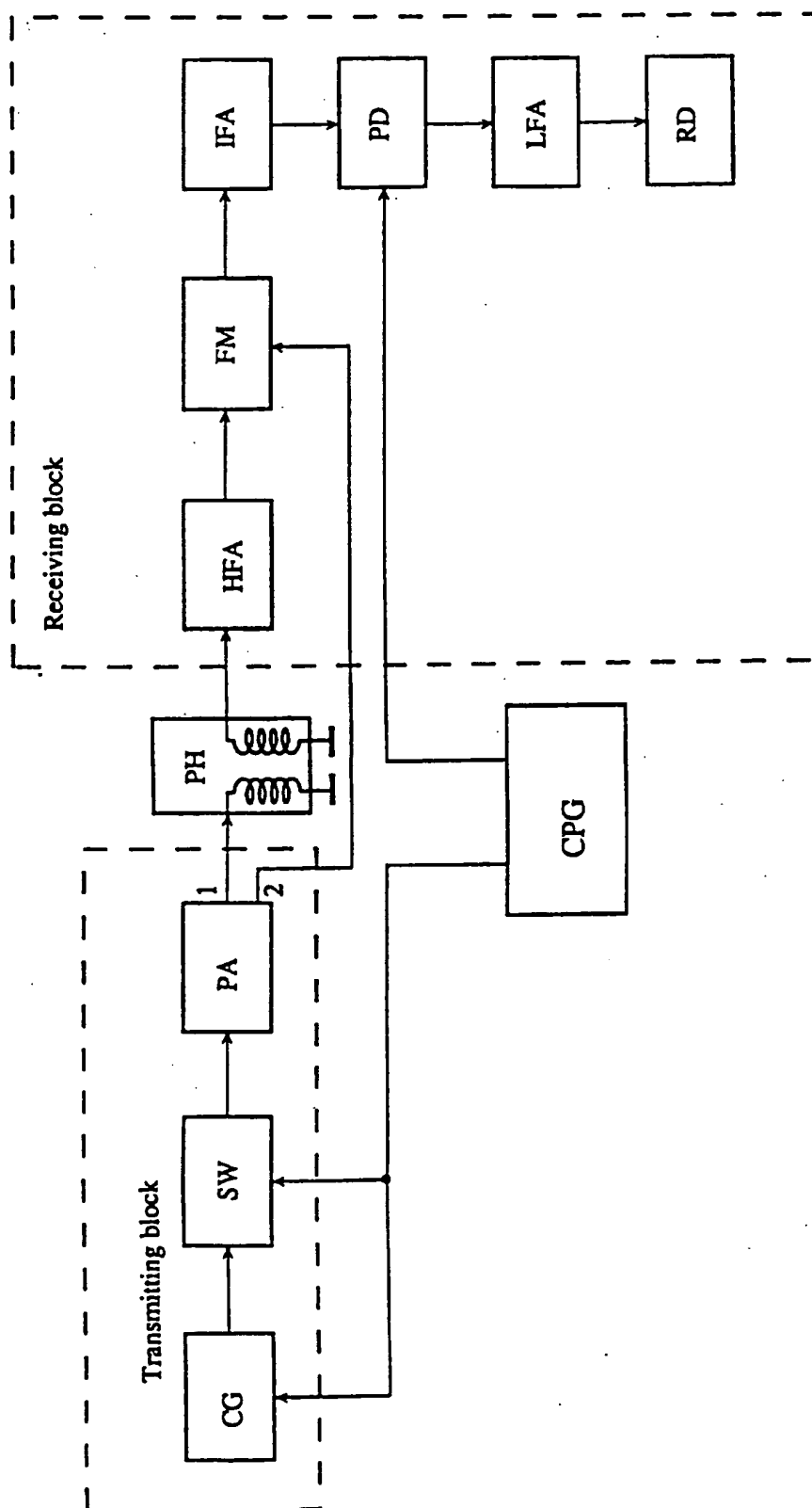


Fig.4

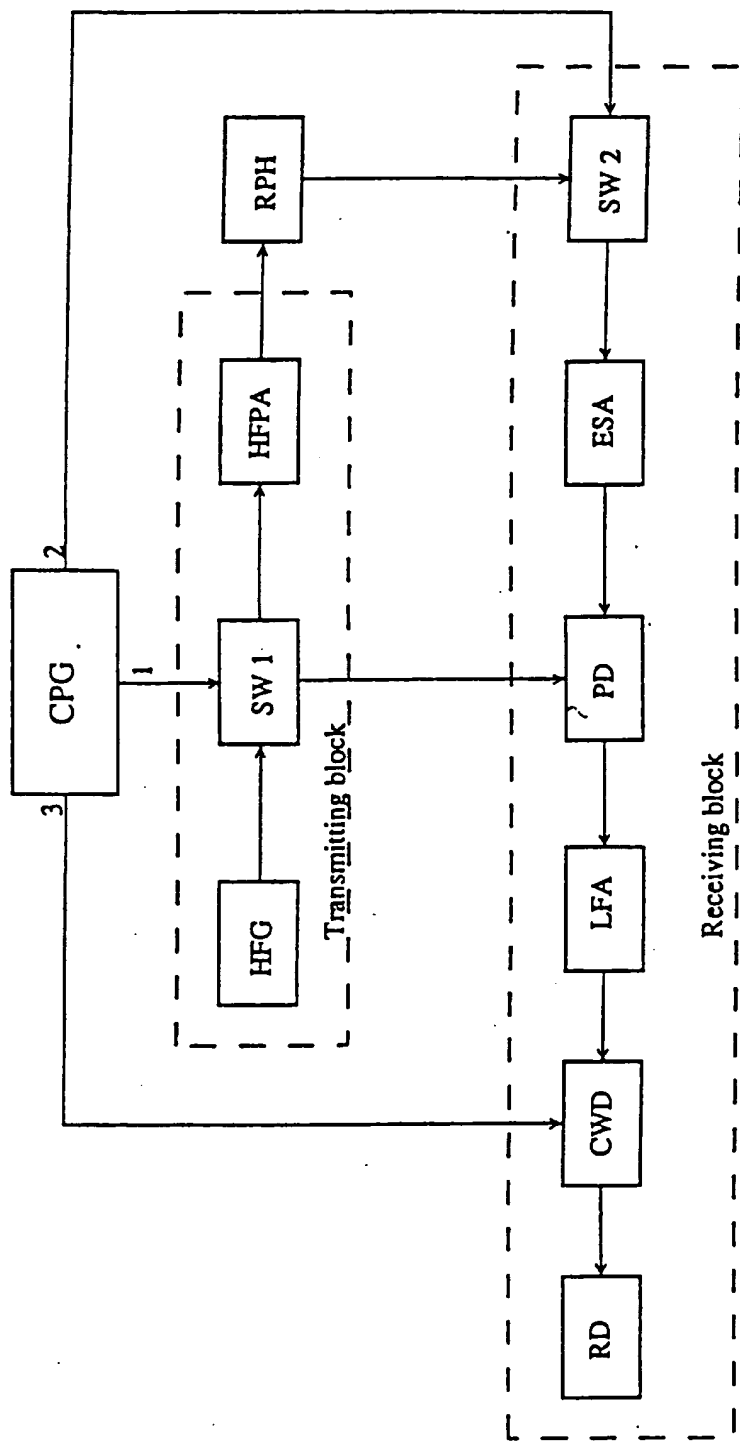


Fig. 6



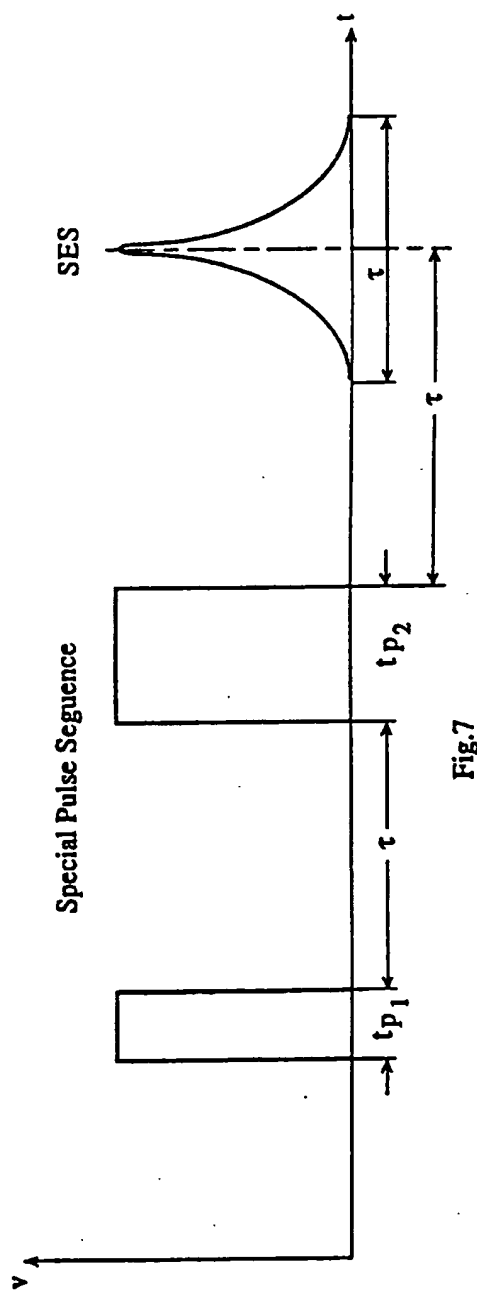
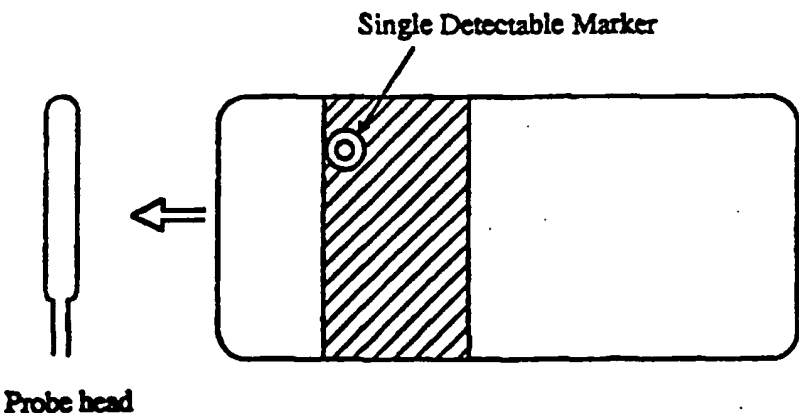


Fig.7



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>G01V 3/14, G06K 19/12, G07D 7/00,</b> <b>G01R 33/44, G01V 15/00</b>	<b>A3</b>	<b>(11) International Publication Number:</b> <b>WO 96/05522</b> <b>(43) International Publication Date:</b> 22 February 1996 (22.02.96)
<b>(21) International Application Number:</b> PCT/EP95/03157 <b>(22) International Filing Date:</b> 9 August 1995 (09.08.95)  <b>(30) Priority Data:</b> 110,597 9 August 1994 (09.08.94) IL  <b>(71) Applicants (for all designated States except US):</b> MICRO TAG TEMED LTD. [IL/IL]; Temed Industrial Park, 86800 D.N. Arava (IL). RAPAPORT, Erich, I. [AT/IL]; 29 Bezalel Street, 64683 Tel Aviv (IL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ROSENFELD, Yuri [IL/IL]; 228/2 Neve Nof, Yeroham (IL). GILL, David [IL/IL]; 12 Rakanati Street, Tel Aviv (IL). GOLDFELD, Lev [IL/IL]; 14/3 Israel Yeshayahu, Beer Sheva (IL). SHAMES, Alexander [IL/IL]; 4/2 King Azzaya, Beer Sheva (IL). LYANDRES, Vladimir [IL/IL]; 8 Dov Yosef Street, Beer Sheva (IL).  <b>(74) Agent:</b> VOSSIUS & PARTNER; Siebertstrasse 4, D-81675 München (DE).	<b>(81) Designated States:</b> AU, BR, CA, JP, NO, NZ, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>  <b>(88) Date of publication of the international search report:</b> 23 May 1996 (23.05.96)	
<b>(54) Title:</b> METHOD FOR LABELING, VERIFICATION AND/OR IDENTIFYING AND DEVICE FOR IMPLEMENTING SAID METHOD  <b>(57) Abstract</b> <p>The invention relates to a method of labeling, authenticating and/or identifying a paper, credit/identification card, bank note, article or any other object using both nuclear magnetic resonance in magnetically ordered materials and nuclear quadrupole resonance phenomena as well as other phenomena of electric/magnetic dipole or tunnel transitions between Stark-Zeeman sublevels, frequencies of which belong to the radio-frequency band. These methods being characterized in that a minor amount of at least one authenticating substance is added to the object, said substance having a strong unique and identifiable response in radio-frequency domain at room temperature, with the spectroscopy being performed in the absence of any supported external static field, and with any specific response (intensity, line width, line shape, splittings, free induction decay, spin echoes or their combinations) being used as a criterion for discrimination. The spectroscopy being performed in time domain (pulse) or frequency domain (continuous wave) with or without intensity, polarization, frequency or any other modulation of the exciting electromagnetic field. The invention also provides instruments for implementing the method, and a set of substances usable with the method.</p> <div style="text-align: center;">  <p>The diagram shows a cross-section of a rectangular sample. A vertical section on the left is shaded with diagonal lines and contains a small circle with a dot in the center, labeled 'Single Detectable Marker'. To the left of this sample is a vertical probe head, also labeled 'Probe head'. An arrow points from the probe head towards the sample.</p> </div>		

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 95/03157

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G01V3/14 G06K19/12 G07D7/00 G01R33/44 G01V15/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G01V G06K G07D G01R G08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 17793 (BRITISH TECHNOLOGY GROUP LIMITED) 15 October 1992 see abstract	1,5,12, 22-25
Y	see page 2, line 3 - page 4, line 22	2-4,6,7, 9,11, 13-15
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

11 April 1996

Date of mailing of the international search report

12.04.96

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 95/03157

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,89 07769 (SCIENTIFIC GENERICS LIMITED) 24 August 1989	2-4,7, 11, 13-15, 40,41
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Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 95/ 03157

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. CLAIMS : 1-39, 42-45
2. CLAIMS : 40,41

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1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
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3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

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☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/EP 95/03157

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